Compensation, interstitial defects and ferromagnetism in diluted semiconductors

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We present a quantitative theory for ferromagnetism in diluted III-V ferromagnetic semiconductors in the presence of the two types of defects commonly supposed to be responsible for compensation: As anti-sites and Mn interstitials. In each case we reduce the description to that of an effective random Heisenberg model with exchange integrals between active magnetic impurities provided by ab initio calculation. The effective magnetic Hamiltonian is then solved by a semi-analytical method (locally self-consistent RPA), where disorder is treated exactly. Measured Curie temperatures are shown to be inconsistent with the hypothesis that As anti-sites provide the dominant mechanism for compensation. In contrast, if we assume that Mn interstitials are the main source for compensation, we obtain a very good agreement between the calculated Curie temperature and the measured values, in both as-grown and annealed samples.

Diluted Magnetic Semiconductors are materials where the interplay of transport and magnetic properties open the perspectives of exciting applications. The III-V semiconductors are particularly promising since a low concentration of magnetic dopants can give relatively high Curie temperatures for ferromagnetism[1, 2]. In these materials it is found that the Curie temperatures depend strongly on methods of preparation and sample history: for the same nominal concentration of magnetic ions the Curie temperature may vary by large factors. Systematic studies show that different annealing treatments display a clear correlation between the Curie temperature and the conductivity. This indicates that the process of magnetic doping is more complex than a straight substitution (Mn(Ga)) of (formally) Ga^{3+} sites by Mn^{2+} atoms, providing a localized magnetic moment and an itinerant hole. In fact the original samples are "compensated", i.e. the density of holes measured by transport is *lower* than the concentration of magnetic ions due to additional donor impurities especially in the samples as grown by Molecular Beam Epitaxy (MBE). The increase in T_C after annealing is then interpreted as removal of the defects, resulting in an increase in the hole concentration which mediates the magnetic exchange. This leaves obscure the precise form of the compensating defect, and does not provide a quantitative theory relating the Mn^{2+} concentration, the hole density and density of compensating defects to ferromagnetism.

There are two probable candidates for compensation: both Arsenic antisites As_{Ga} (i.e. As atoms on sites of the Ga sub-lattice) and Mn interstitials Mn_I have long been known to be double donors. The two forms of defects differ in an important way: for each As_{Ga} there are two holes removed, i.e. only the carrier density is changed, while each interstitial, in addition, introduces a magnetic moment, changing the number of magnetically active ions. Microscopic calculations indicate that the Mn_I are preferentially situated on interstitial sites adjacent to occupied Mn(Ga) and that the coupling between interstitials and the adjacent moment is essentially given by antiferromagnetic superexchange coupling (J ≈ -320 K) [3]. In fact there are two inequivalent interstitial positions, the Mn atom can be located inside the tetrahedron formed by either four Ga $T(Ga_4)$ or else four As $T(As_4)$. We shall make no distinction between the two possible positions sites, since in either case the AF exchange with Mn(Ga) is strongly antiferromagnetic, and we refer to Mn_I as the sum of the two.

The immediate question is, what is the proportion of the two defects: interstitials Mn_I and As_{Ga} in the ferromagnetic samples? A conclusion of this paper is that the observed Curie temperatures in samples at different stages of annealing, can *only* be explained assuming that interstitial defects dominate compensation. Such a dominance agrees with Wolos et al. [4], who estimated, from the strength of optical transitions, a relatively small (fewer than 10% of the total Manganese atoms) number of antisites As_{Ga}, fewer than 10% of the total Manganese atoms, and, from Electron Paramagnetic Resonance, a much larger number of other compensating defects. Similarly Wang et al [5] showed that the saturated magnetization at low temperatures was consistent with the elimination of *two* magnetic moments with each impurity. Furthermore polarised neutrons reflectometry [6] and Auger spectroscopy and resistivity measurements [2] showed that the annealing process corresponds to redistribution of Mn sites and the increase of the magnetisation far from the surface. We emphasise that clear proof of the rôle of interstitials is still necessary, as other

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techniques, by Transmission Electron Micrography[7], or by Infrared Absorption and Positron Annihilation Spectroscopy [8] suggested a much higher concentration of anti-sites. The new element we are bringing here, is a *quantitative* theory for the Curie temperature, which as we shall explain below, is much more accurate than Zener mean-field theory. We note that in ref [9] we anticipated the fact that the changes in the carrier density due solely to anti-sites were *insufficient* to explain the reduction of T_C.

Recently, by combining first principles calculations and an semi-analytical approach, we were able to provide an excellent agreement between the calculated Curie temperatures and those measured in optimally doped semiconductors [9]. In the first step of this method, we derive the exchange integrals between magnetic impurities using the Local Density Approximation (TB-LMTO) and magnetic force theorem [10] providing an effective classical random Heisenberg Hamiltonian. Note that the calculated exchange integrals, include the effect of disorder within a Coherent Potential Approximation (CPA) for electronic motion. In the second step, we treat the random effective Heisenberg model within an approach where thermal fluctuations are treated within a local random phase appoximation (RPA), whilst the disorder is treated '*exactly*', i.e. the magnetic properties are calculated for individual configuration of disorder generated by sampling techniques. This theory is an extension of ref.[11] where disorder in the *effective* Hamiltonian was treated by a form of CPA. An attractive feature of an "exact" treatment of disorder is that it allows us, for example, to study the effect of correlations in the disorder [12], a question of importance in interpreting experiments on high Curie-temperature samples grown using the OMVPE technique (Organo-Metallic Vapor Phase Epitaxy) [13]. We attribute the success of our approach to (i) the realistic calculations of the exchange integrals (ii) to a proper treatment of the thermal fluctuations and disorder of the effective Heisenberg Hamiltonian. This second point is confirmed by consistency with Monte-Carlo simulations [14].

We first analyze the dependence of the Curie temperature T_C with the density of As anti-sites $y_{\bar{\rm As}}$. As in our preliminary study of this issue[9], which was restricted to a single nominal concentration of Mn, we do this by introducing in the ab-initio stage of our calculation a concentration of anti-sites, which influences the calculated exchange couplings. This calculation also allows us to verify, within LDA that there is indeed the compensation expected. In Fig. 1 we plot, for different concentration $x_{\rm Mn}$ of Mn, the variation of the calculated T_C in $(Ga_{1-x_{\rm Mn}-y_{\bar{\rm As}}}Mn_{x_{\rm Mn}}\bar{\rm As}_{y_{\bar{\rm As}}})$As as a function of $\gamma = n_h/x_{\rm Mn}$. Since each As anti-site is a double donor, the carrier density is $n_h = x_{\rm Mn} - 2y_{\bar{\rm As}}$. We observe that above a critical value $\gamma_c(x_{\rm Mn})$, T_C is weakly sensitive to As-antisites, this is particularly clear for $x_{\rm Mn} = 0.03$ and 0.05. For 7% Mn, for example, we also observe that for $\gamma < 0.50$ ferromagnetism is unstable. The reason for this is that as the density decreases, the nearest neighbour exchange integral becomes increasingly dominated by the (antiferromagnetic) superexchange contribution, leading to frustration. Note also that this behaviour with hole density is incompatible with Zener mean-field theory which predicts that $T_C \propto n_h^{1/3}$. Let us now discuss the compatibility of these results with the assumption that As anti-sites dominate the mechanism of compensation. We do this by comparing samples with approximately fixed total density of Mn impurities but exhibiting large variation in their Curie temperatures.

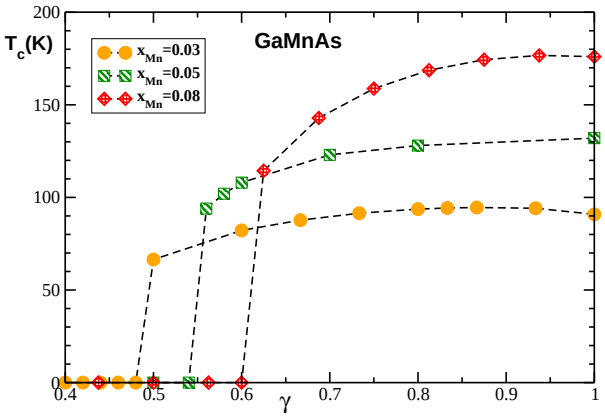

FIG. 1: Effect of As anti-sites on T_C in $(Ga_{1-x_{\rm Mn}-y_{\bar{\rm As}}}Mn_{x_{\rm Mn}}As_{y_{\bar{\rm As}}})$As for different Mn concentation. The carrier density is $n_h = x_{\rm Mn} - 2y_{\bar{\rm As}}$ and $\gamma = \frac{n_h}{x_{\rm Mn}}$.

We plot in Fig. 2, the measured T_C^{exp} as a function of $\gamma = n_h/x_{\rm Mn}$. In contrast to calculated values, T_C^{exp} is more sensitive to the carrier density, varying linearly with γ. The other important difference with the curves in Fig.1 is that ferromagnetism is still observed for rather small values of γ. Thus, if we assume that As anti-sites dominate compensation, theory and experiment would disagree. As our approach was successful for uncompensated samples, and consistent with Monte-Carlo[14] we conclude that As anti-sites do *not* dominate compensation.

As already mentioned, the saturated magnetization[5] at low temperature indicates that the compensating defects affect both the density of carriers and the density of magnetically active Mn impurities. Let us now take the alternate limit in which compensation is taken to be *entirely* due to the presence of Mn interstitial defects Mn_I. We denote by $x_{\rm Mn}$, $x_{\rm Mn_{Ga}}$ and $x_{\rm Mn}$(I) respectively, the total density of Mn, the density of Mn on Ga sublattice and on interstitial location respectively. Recent

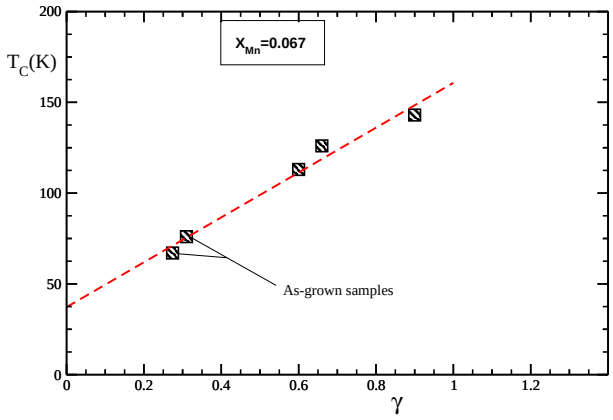

FIG. 2: Experimental values of T_C ([2]) as a function of the measured hole density per magnetic impurity $\gamma = \frac{n_h}{x_{\rm Mn}}$ for $Ga_{1-x}Mn_xAs$ at nominal concentration 6.7%.

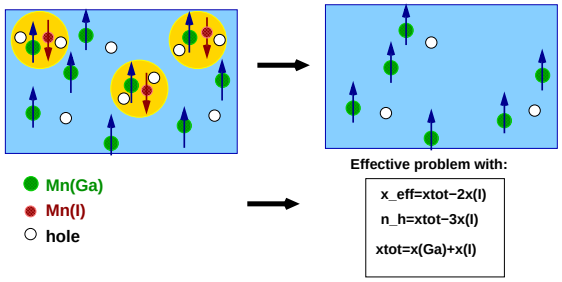

FIG. 3: Left side: the up (resp. down) arrows indicate spin of Mn(Ga) (resp. Mn_I). The small circles are itinerant carrier (holes). Mn_I are double donor and strongly coupled antiferromagnetically to $Mn_{\rm Ga}$. Right side: effective model with $x_{\rm eff}$ $Mn_{\rm Ga}$ impurities and n_h holes.

first principle calculations [3] and channeling Rutherford backscattering experiments [15] indicates that Mn interstitials are preferably attracted by $Mn_{\rm Ga}$ and tend to form pairs of spins with strongly antiferromagnetic couplings. Thus, we suppose that Mn_I are not completely random, but are only in positions with a $Mn_{\rm Ga}$ as a nearest neighbour (see fig. 3). In writing an effective Hamiltonian, we will eliminate the strongly antiferromagnetically coupled pairs of the Mn_I and adjacent $Mn_{\rm Ga}$. They can be assumed, within high precision, to form bound singlet pairs whose effect on the magnetically active ions is small[16]. The remaining "active" Mn of density $x_{\rm eff} = x_{\rm Mn} - 2x_{\rm Mn}(\rm I)$ which are *not* directly coupled to a Mn_I, and with the measured carrier density n_h, interact via an effective Heisenberg model with couplings determined by the measured carrier density n_h. We make the same calculation as before but with the effective concentration $x_{\rm eff}$ and compensation γ_{eff}. Since each Mn_I is a double donor, the total density of carriers is $n_h = x_{\rm Mn(Ga)} - 2x_{\rm Mn}(\rm I) = x_{\rm Mn} - 3x_{\rm Mn}(\rm I)$. Thus from each measured n_h we can deduce the density of Mn_I and of 'unpaired' Mn which are, respectively, $x_{\rm Mn}(\rm I) = \frac{1}{3}(x_{\rm Mn} - n_h)$ and $x_{\rm eff} = \frac{1}{3}(x_{\rm Mn} + 2n_h)$. We also define the effective γ parameter as $\gamma_{\rm eff} = \frac{n_h}{x_{\rm eff}} = \frac{3n_h}{x_{\rm Mn}+2n_h}$.

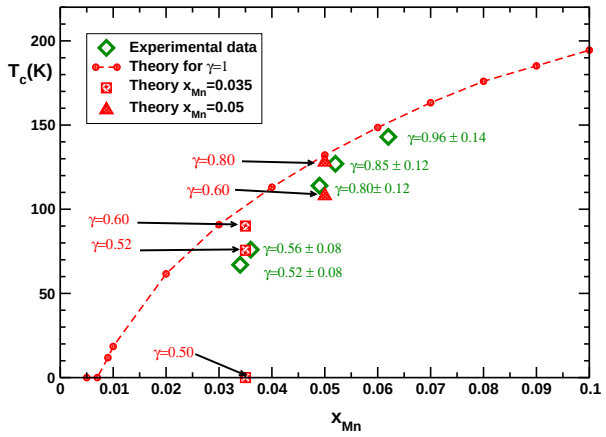

FIG. 4: T_C for $Mn_xGa_{1-x}As$. The experimental data (diamonds) are plotted assuming for each sample $x_{\rm Mn} = x_{\rm eff}$ and $\gamma = \gamma_{\rm eff}$ (see text). The values of $\gamma_{\rm eff}$ are shown in the figure. The small circles , the square and triangles are calculated Curie temperature. The small circles (dashed line) correspond to uncompensated samples $\gamma = 1$ and the square and triangle correspond to $x_{\rm Mn} = 0.035$ and 0.05 respectively. For these cases, the value of γ is shown in the figure.

In Fig.4 we show both the experimental data and calculated Curie temperature for various γ as a function of $x_{\rm Mn} = x_{\rm eff}$. The variable $x_{\rm eff}$ are calculated from the values given in [2] and the corresponding values of $\gamma_{\rm eff}$ is noted on the figure for each sample. We take the $x_{\rm Mn}$ to be the nominal concentration of each sample; thus we neglect effects of surface inhomogeneities[4, 5, 6] in calculating the *bulk* ordering temperature. First, we observe that the well annealed samples (of highest T_C) are in excellent agreement with the calculated values for uncompensated samples, $\gamma = 1$ curve ('optimal curve'). We remark that this optimal curve, which depends on exchange integrals recalculated for each concentration, can nevertheless be well parameterized by the simple form, up to $x_{\rm Mn} = 0.10$, $T_C \approx A(x_{\rm Mn} - x_c)^{1/2}$ where $x_c = 0.0088$, $A = 649\ K$ for Ga(Mn)As. The samples corresponding

to intermediate T_C are still in reasonable agreement with the optimal curve for uncompensated samples at the *effective* concentration of magnetically active ions. The deviation from this optimal line is small but increasingly visible for as-grown samples. In order to refine our calculations we have taken into account that for these samples $\gamma_{\rm eff}$ is substantially less than 1. We therefore performed additional calculations for fixed $x_{\rm Mn} = 0.035$ and 0.05 and various hole densities. As in Fig. 1, we vary $\gamma_{\rm eff}$ in this effective Hamiltonian with the addition of anti-sites, here used as a purely calculational device to change the carrier density, whilst keeping the calculation fully self-consistent. We now observe that the agreement with the experimental measurements is very good for all the measured samples (as-grown and annealed). For example the as-grown sample which corresponds to $x_{\rm eff} \approx 0.035$ and $\gamma_{\rm eff} \approx 0.52$ agrees very well with the calculated value (square symbol) for the same parameters. Note that using the above relations we find that the density of Mn_I in as-grown samples is $x_{\rm Mn}({\rm I}) \approx 0.016$ which corresponds to approximately 25% of the total Mn density. This is in very good agreement with the value estimated in ref.[17] (see Fig.4 of ref.[17]).

In conclusion, we have shown that experimental measurements in samples with fixed nominal magnetic impurity concentration could not be explained assuming As anti-sites as the dominant mechanism for compensation. On the other hand, with the assumption that Mn interstitials dominate, we obtained an excellent quantitative agreement with the measured T_C in both as-grown and annealed samples. It may be possible, in varying sample preparation, to increase the number of anti-sites, this will have a weak effect on the T_C, provided the γ_{eff} remains above the region of instability, as seen in Figure 1. For Ga(Mn)As samples, we can write an explicit first approximation ($\gamma_{\rm eff} = 1$) using the empirical form for the optimal curve, by replacing $x_{\rm Mn}$ by $x_{\rm eff}$: $T_C \approx A(\frac{x_{\rm Mn}+2n_h}{3} - 0.0088)^{1/2}$ where $A = 649\ K$. To take into account the smaller corrections due to the value of $\gamma_{\rm eff}$ we do not have an explicit analytical form, but numerical corrections can be predicted as in Figure 1. Hence our combined ab-initio/local-RPA approach is a very powerful tool to study ferromagnetism in diluted ferromagnetic systems even in the presence of compensating defects. The same approach can be applied to macroscopic inhomogeneities, for example surface effects, which may be necessary to understand thin films and devices.

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